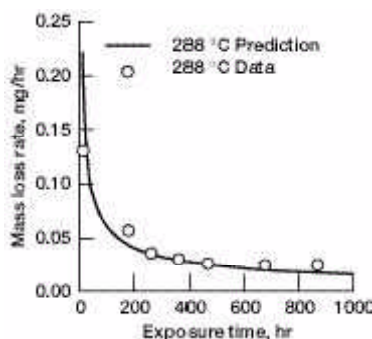


# Long-Term Durability of a Matrix for High-Temperature Composites Predicted

Polymer matrix composites (PMC's) are being increasingly used in applications where they are exposed for long durations to harsh environments such as elevated temperatures, moisture, oils and solvents, and thermal cycling. The exposure to these environments leads to the degradation of structures made from these materials. This also affects the useful lifetimes of these structures. Some of the more prominent aerospace applications of polymer matrix composites include engine supports and cowlings, reusable launch vehicle parts, radomes, thrust-vectoring flaps, and the thermal insulation of rocket motors. This demand has led to efforts to develop lightweight, high-strength, high-modulus materials that have upper-use temperatures over 316 °C.

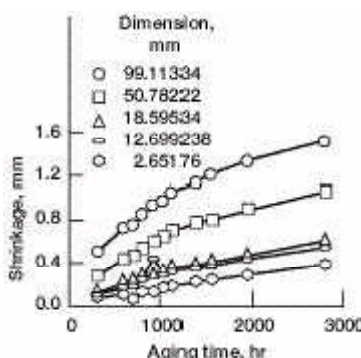
A cooperative program involving two grants to the Massachusetts Institute of Technology and in-house work at the NASA Glenn Research Center was conducted to identify the mechanisms and the measurement of mechanical and physical properties that are necessary to formulate a mechanism-based model for predicting the lifetime of high-temperature polymer matrix composites. The polymer that was studied was PMR-15 polyimide, a leading matrix resin for use in high-temperature-resistant aerospace composite structures such as propulsion systems. The temperature range that was studied was from 125 to 316 °C.

The diffusion behavior of PMR-15 neat resin was characterized and modeled. Thermogravimetric analysis (TGA) was also conducted in nitrogen, oxygen, and air to provide quantitative information on thermal and oxidative degradation reactions. A new low-cost technique was developed to collect chemical degradation data for isothermal tests lasting up to 4000 hr in duration. In the temperature range studied, results indicate complex behavior that was not observed by previous TGA tests, including the presence of weight-gain reactions. These were found to be significant in the initial periods of aging from 125 to 225 °C. Two types of weight loss reactions dominated at aging temperatures above 225 °C. One was concentrated at the surface of the polymer and was very active at temperatures above 225 °C. The second was observed to dominate in the latter stages of aging at temperatures below 260 °C. This three-reaction model satisfactorily explains past findings that the degradation mechanism of PMR-15 appears to change around 316 °C. It also indicates that the second weight gain mechanism is a significant factor at temperatures below 204 °C. On the basis of these results, a predictive model was developed for the thermal degradation of PMR-15 at 316 °C. A comparison of data generated by this model with actual experimental data is shown in the following figure.



*Comparison of model-generated and experimental data for the decomposition of PMR-15 at 316 °C.*

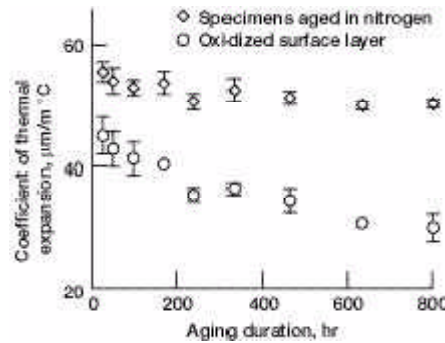
Tests were also conducted at Glenn to further elucidate the theory of a three-mechanism degradation model. PMR-15 specimens were aged in air at 204, 260, 288, and 316 °C for times as long as 4400 hr. Specimens of four different volume/surface areas were studied to evaluate geometrical effects. Weight loss and dimensional changes were measured--3 length, 4 width, and 10 thickness measurements for each specimen. The surface layer thickness was measured at predetermined intervals. The study confirmed that a three-mechanism degradation model is appropriate. Also, it indicates that other mechanisms may be operating. The weight loss was shared by both the oxidizing surface and the thermally degrading central core material. The ratios were dependent on the test temperature. The surface loss diminished as the temperature was reduced, and the core loss remained about the same. Dimensional shrinkage partitioning between the surface and the bulk polymer followed the same course. The next figure presents the progression of shrinkage with aging time for different dimensions of PMR-15 neat resin specimens aged at 316 °C.



*Dimensional changes as a function of aging time and temperature for PMR-15 neat resin specimens during aging at 316 °C.*

Thermo-oxidative aging produces a nonuniform degradation state in PMR-15. A surface layer, usually attributed to oxidative degradation, forms. This surface layer has different properties than the central core material. A set of material tests was designed to separate the properties of the oxidized surface layer from the properties of the inner material. Test specimens were aged at 316 °C in either air or nitrogen for up to 800 hr. The thickness of the oxidized layer, the dimensional shrinkage, and the coefficient of thermal expansion were measured directly. The coefficient of thermal expansion data are shown in the final figure. The nitrogen-aged specimens were assumed to be representative of thermally aged

PMR-15 and, therefore, have the same properties as the interior material in the air-aged specimens. Four-point bend tests were performed to measure the flexural modulus of both the surface layer and the inner material. Innovative bimetallic strip specimens were machined from thick aged specimens and tested to determine surface layer shrinkage and coefficient of thermal expansion.



*Effects of aging time on the coefficient of thermal expansion on the bulk and oxidized surface layer of PMR-15 neat resin.*

Results show that the surface layer is under tension at the cure temperature and under compressive loading at room temperature. This confirms a previous report that showed that surface cracking of PMR-15 occurs while at elevated temperature and is not due to thermal cycling during specimen weighing operations. These physical properties are of valuable use in modeling the durability and lifetime of PMR-15 structural elements because they are not readily found in the literature.

The data gained from these studies present a new understanding of the degradation of all polyimide-type composite matrices. The results from this cooperative effort are of significant importance to the development of new composite materials for advanced aerospace propulsion systems.

**Find out more about this research.**

(<http://www.grc.nasa.gov/WWW/MDWeb/5150/Polymers.html>)

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